3. Thermodynamic Properties:

In the previous chapter we concluded that the Meissner-Ochsenfeld effect of a superconductor guarantees that its states are path independent and, thus, are uniquely characterised by both the temperature T and the magnetic induction $\vec{B}$. This allows to apply the useful concepts of thermodynamics to describe a superconductor.

3.1 Fundamental Idea:

A macroscopic physical system consists of a huge number of independent degrees of freedom of its individual particles. But despite of that thermodynamics yields a reduced description with just a few macroscopic system variables.

Thermodynamics can deal with the following problems. It describes system properties from a macroscopic point of view, for instance, it can provide conditions for the stability of a phase. It particular, it deals with the equilibrium properties of a system, which emerge under certain experimental conditions. Note that experimentally an equilibrium is reached only quite slowly as it involves adiabatic parameter changes and free exchanges, for instance, of energy and particles with the environment. Therefore, thermodynamic statements about an equilibrium state are, in principle, completely independent from the practical question how to realise it experimentally.

Such problems in thermodynamics are discussed by analyzing a thermodynamic potential. To this end, one generically proceeds as follows:

1) Find the thermodynamic variables, which uniquely characterise a system state.
2) Find the thermodynamic potential, which has the independent variables from 1) as natural variables.
3) Equilibrium states are characterised by extremizing the thermodynamic potential.
4) Two phases are in equilibrium provided that the thermodynamic potentials of both phases are equal.

In the following we apply this procedure to describe a superconductor within the realm of thermodynamics.

3.2 Thermodynamic Potential:

We start with the thermodynamic description by involving the basic relation for reversible processes, which consists of combining the first and second law of thermodynamics:

$$dU = T\,dS - P\,dV + \mu_0 H\, d(VM) \qquad (3.1)$$

Here we determine the change of the inner energy dU by adding products of the intensive variables (T, P, H) with the total differentials of the respective extensive variables (S, V, VM). Note that M denotes here the magnetization, i.e. the magnetic moment per volume, so VM represents the magnetic moment of the material, which is extensive. Furthermore, we remark that we assume the systemegoistic convention, i.e. whatever is good for the system is counted positively. For instance, the inner energy U increases (decreases) for increasing (decreasing) the magnetization M of a paramagnet (diamagnet). Or in other words: For a paramagnet (diamagnet) magnetic field energy is built up (reduced) due to an increase (decrease) of the magnetization $dM > 0$ ($dM < 0$), involving the magnetization work $\mu_0 H\, d(VM) > 0$ ($\mu_0 H d(VM) < 0$) being put into (freed from) the system.

We conclude from (3.1) that the inner energy U is a thermodynamic potential, which has the extensive variables (S, V, VM) as the natural variables

$$U = U(S, V, M) \qquad (3.2)$$

This means that the respective intensive variables (T, P, H) follow from differentiations:

$$T = \frac{\partial U}{\partial S}\bigg|_{V,M}, \quad P = -\frac{\partial U}{\partial V}\bigg|_{S,M}, \quad H = \frac{1}{V\mu_0}\frac{\partial U}{\partial M}\bigg|_{S,V} \qquad (3.3)$$

But both the entropy S and the magnetization M are physical quantities, which are not directly accessible in the laboratory. Therefore, it is advantageous to switch the description from the extensive variables S, VM to their canonically conjugated intensive variables T, H. This is accomplished by performing a double Legendre transformation from the inner energy U to the (magnetic) free enthalpy, which is also called (magnetic) Gibbs free energy

$$G = U - TS - \mu_0 H V M \tag{3.4}$$

For the total differential of (3.4) we conclude by taking into account (3.1)

$$dG = -S dT - P dV - \mu_0 V M dH \tag{3.5}$$

Thus, G is now a thermodynamic potential, which has (T, V, H) as the natural variables

$$G = G(T, V, H) \tag{3.6}$$

The canonically conjugated variables follow again from differentiations:

$$S = -\left.\frac{\partial G}{\partial T}\right|_{V,H}, \quad P = -\left.\frac{\partial G}{\partial V}\right|_{T,H}, \quad M = -\frac{1}{\mu_0 V}\left.\frac{\partial G}{\partial H}\right|_{T,V} \tag{3.7}$$

In the following we simplify the thermodynamic discussion by assuming a normal conductor or a superconductor, whose volume does not change:

$$dV = 0 \tag{3.8}$$

Thus, we consider the volume V from now on as a fixed dummy thermodynamic variable, which can be ignored due to its redundancy. This reduces (3.5) to

$$dG = -S dT - \mu_0 V M dH \tag{3.9}$$

so the free enthalpy G in (3.6) turns out to be only a function of the temperature T and the magnetic field H alone

$$G = G(T, H) \tag{3.10}$$

Then the entropy S and the magnetization follow from

$$S = -\left.\frac{\partial G}{\partial T}\right|_{H} \tag{3.11}$$

$$M = -\frac{1}{\mu_0 V}\left.\frac{\partial G}{\partial H}\right|_{T} \tag{3.12}$$

Within this framework we characterise now the free enthalpy of a normal and a superconductor.

3.3 Free Enthalpy of Both Phases:

In Chapter 2 we stated that a superconductor is characterized by the Meissner-Ochsenfeld effect. This implies for the magnetization

$$B = \mu_0 (H + M) \overset{!}{=} 0 \implies M(H) = -H \tag{3.13}$$

Taking into account (3.13) we now integrate isothermally (3.12) from $(T, 0)$ to (T, H), yielding for the free enthalpy of the superconductor:

$$G_s(T, H) = G_s(T, 0) + \frac{\mu_0}{2} V H^2 \tag{3.14}$$

Thus, the temperature independence of the magnetization (3.13) has the consequence that the entropy of the superconductor does not depend on the magnetic field H:

$$S_s(T, H) \overset{(3.11)}{=\!=} -\left.\frac{\partial G_s(T,H)}{\partial T}\right|_H \overset{(3.14)}{=\!=} -\left.\frac{\partial G_s(T,0)}{\partial T}\right|_H \overset{(3.11)}{=\!=} S_s(T, 0) \tag{3.15}$$

A subsequent differentiation of the entropy S with respect to the temperature T yields the heat capacity C:

$$C = T \left.\frac{\partial S}{\partial T}\right|_H \tag{3.16}$$

Indeed, differentiating the double Legendre transformation (3.4) with respect to the temperature T yields

$$\left.\frac{\partial G}{\partial T}\right|_H = \left.\frac{\partial U}{\partial T}\right|_H - S - T\left.\frac{\partial S}{\partial T}\right|_H - \mu_0 V H \left.\frac{\partial M}{\partial T}\right|_H \tag{3.17}$$

so we conclude that the heat capacity

$$C = \left.\frac{\partial U}{\partial T}\right|_H \tag{3.18}$$

reduces due to the entropy (3.11) and the magnetization (3.13) to (3.16). Thus, we read off from (3.15) and (3.16) that also the heat capacity of a superconductor turns out to be independent of the magnetic field H:

$$C_s(T, H) \overset{(3.16)}{=\!=} T\left.\frac{\partial S_s(T,H)}{\partial T}\right|_H \overset{(3.15)}{=\!=} T\left.\frac{\partial S_s(T,0)}{\partial T}\right|_H \overset{(3.16)}{=\!=} C_s(T, 0) \tag{3.19}$$

Correspondingly, a normal conductor, which is paramagnetic, is characterized by an approximately vanishing magnetization:

$$M = 0 \tag{3.20}$$

An isothermal integration of (3.12) with (3.20) from $(T, 0)$ to (T, H) thus yields

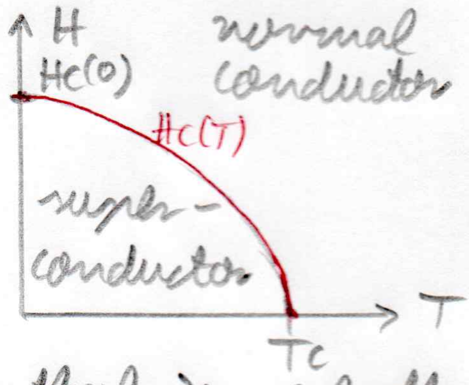
$$G_n(T,H) = G_n(T,0) \qquad (3.21)$$

This means that the free enthalpy of a normal conductor does not depend on the magnetic field H. As a consequence we obtain also for the normal conductor that both its entropy and its heat capacity do not depend on the magnetic field H:

$$S_n(T,H) \overset{(3.11)}{=\!=} -\frac{\partial G_n(T,H)}{\partial T}\Big|_H \overset{(3.21)}{=\!=} -\frac{\partial G_n(T,0)}{\partial T}\Big|_H \overset{(3.11)}{=\!=} S_n(T,0) \qquad (3.22)$$

$$C_n(T,H) \overset{(3.16)}{=\!=} T\frac{\partial S_n(T,H)}{\partial T}\Big|_H \overset{(3.22)}{=\!=} T\frac{\partial S_n(T,0)}{\partial T}\Big|_H \overset{(3.16)}{=\!=} C_n(T,0) \qquad (3.23)$$

3.4 Consequences from Critical Line:



Along the critical curve $H_c(T)$ in the H-T plane of control parameters an equilibrium exists between the normal conducting phase and the superconducting phase. According to the basic laws of thermodynamics this implies that the free enthalpies of both phases have to be equal along this critical curve:

$$G_s(T, H_c(T)) = G_n(T, H_c(T)) \qquad (3.24)$$

This implies due to (3.14) and (3.21)

$$G_s(T,0) + \frac{\mu_0}{2} V H_c(T)^2 = G_n(T,0) \qquad (3.25)$$

At first, we conclude from (3.25) for $T \leq T_c$:

$$G_n(T,0) - G_s(T,0) \geq 0 \qquad (3.26)$$

This means that the free enthalpy of the superconducting phase is smaller than the corresponding one of the normal conducting phase. Thus, it is energetically more favourable to realise the superconducting phase. Secondly, (3.25) implies that the entropy (3.15) and the heat capacity (3.19) of the superconductor follow from the corresponding quantities of the normal conductor (3.22), (3.23) and the critical curve $H_c(T)$. This is investigated in more detail in the next two sections. There we will see that properties of $H_c(T)$ have thermodynamic consequences and, conversely, thermodynamics has implications for $H_c(T)$.

3.5 Entropy:

Inserting (3.25) into (3.15) yields together with (3.22)

$$S_s(T,0) = S_n(T,0) + \mu_0 V H_c(T) \frac{\partial H_c(T)}{\partial T} \qquad (3.27)$$

At zero temperature the third law of thermodynamics holds, which implies

$$S_s(0,0) = S_n(0,0) \qquad (3.28)$$

Thus, as $H_c(0) \neq 0$, we read off from (3.27) at zero temperature

$$\lim_{T \downarrow 0} \frac{\partial H_c(T)}{\partial T} = 0 \qquad (3.29)$$

This means that the critical line $H_c(T)$ must have a horizontal tangent at $T=0$.

In the temperature range from zero temperature to the critical temperature we know that the critical line $H_c(T)$ has a negative slope:

$$\frac{\partial H_c(T)}{\partial T} < 0 \, , \quad 0 < T < T_c \qquad (3.30)$$

This implies for the latent heat

$$\Delta Q = T \left\{ S_n(T,0) - S_s(T,0) \right\} \qquad (3.31)$$

that it is always positive:

$$\Delta Q \overset{(3.27),(3.31)}{=} -\mu_0 V T H_c(T) \frac{\partial H_c(T)}{\partial T} \overset{(3.30)}{>} 0 \, , \quad 0 < T < T_c \qquad (3.32)$$

Thus, at the transition from a normal to a superconductor heat is freed and a first-order phase transition occurs.

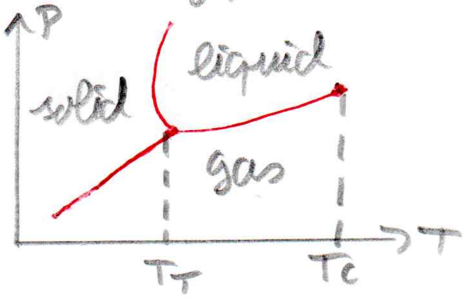
~~Note that~~ (3.32) can be reformulated according to

$$\Delta Q = \mu_0 V \left[0 - H_c(T) \right] T \frac{\partial H_c(T)}{\partial T} > 0 \qquad (3.33)$$

so that it becomes transparent that it represents an analogue of the seminal Clausius-Clapeyron relation for the transition line between a gas and a liquid:

$$\frac{\partial P}{\partial T} = \frac{S_g - S_\ell}{V_g - V_\ell} \Rightarrow \Delta Q = T(S_g - S_\ell) = (V_g - V_\ell) T \frac{\partial P}{\partial T} > 0 \qquad (3.34)$$

Thus, the positivity of the latent heat ΔQ is guaranteed for the gas-liquid transition (3.34) due to $V_g - V_\ell > 0$ and $\partial P / \partial T > 0$,



whereas for the normal conductor – superconductor transition (3.33) we have that the difference of magnetizations $0 - H_c$ is negative and also the slope $\partial H_c(T)/\partial T$ is negative.

Finally, let us evaluate (3.32) at the critical temperature $T = T_c$. From experimental observations we know on the one hand that there occurs a second order phase transition, i.e. the latent heat must vanish

$$\Delta Q = 0 \quad \text{at } T = T_c \tag{3.35}$$

On the other hand, the critical curve $H_c(T)$ for $T \leq T_c$ is found to be a smoothly differentiable function with the properties that at $T = T_c$ the critical magnetic field vanishes, i.e.

$$H_c(T_c) = 0 \tag{3.36}$$

with a finite slope, i.e.

$$\left.\frac{\partial H_c(T)}{\partial T}\right|_{T=T_c} \text{finite} \tag{3.37}$$

Thus, we conclude that (3.36) and (3.37) immediately imply (3.35) due to (3.32).

3.6 Heat Capacity:

Inserting (3.27) into (3.19) yields together with (3.23) for the specific heat

$$C_s(T,0) = C_n(T,0) + \mu_0 V T \left\{ H_c(T) \frac{\partial^2 H_c(T)}{\partial T^2} + \left[\frac{\partial H_c(T)}{\partial T}\right]^2 \right\} \tag{3.38}$$

Thus, evaluating (3.38) at the critical temperature, we obtain from (3.36) and a finite curvature of the critical $H_c(T)$ at $T = T_c$, i.e.

$$\left.\frac{\partial^2 H_c(T)}{\partial T^2}\right|_{T=T_c} \text{finite} \tag{3.39}$$

that the difference of the heat capacities of a normal and a superconductor follows the Rudgers formula

$$C_s(T_c,0) - C_n(T_c,0) = \mu_0 V T_c \left[\left.\frac{\partial H_c(T)}{\partial T}\right|_{T=T_c} \right]^2 > 0 \tag{3.40}$$

Thus, at the critical temperature $T = T_c$ the heat capacity makes a jump, which is characteristic for a second phase transition. And from the magnitude of that jump one can deduce the slope of the critical curve $H_c(T)$ at $T=T_c$ according to (3.40).

3.7 Rok Formula:

A good empirical approximation for the critical line $H_c(T)$ is provided by the Rok formula

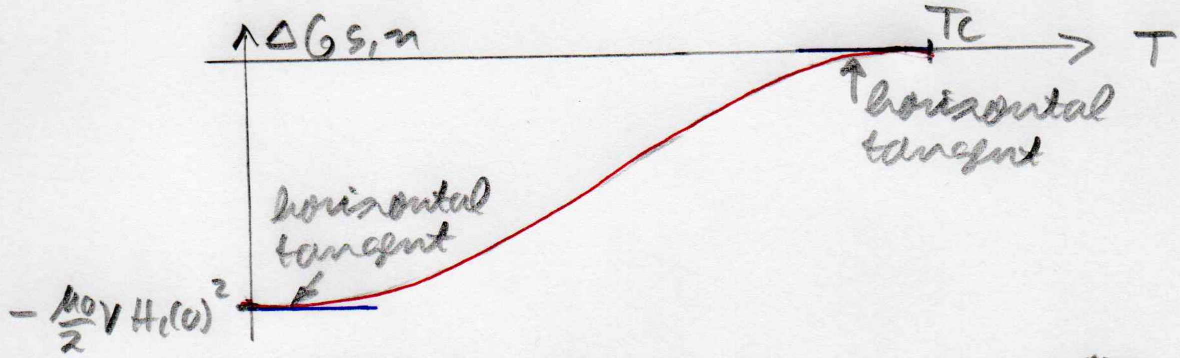
$$H_c(T) = H_c(0)\left[1-\left(\frac{T}{T_c}\right)^2\right] \qquad (3.41)$$

With this we can conveniently calculate the differences for the enthalpy, the entropy, and the heat capacity in the normal and the superconducting phase.

3.7.1 Free Enthalpy:

The difference of the respective free enthalpies follows from (3.25) and (3.41) to be

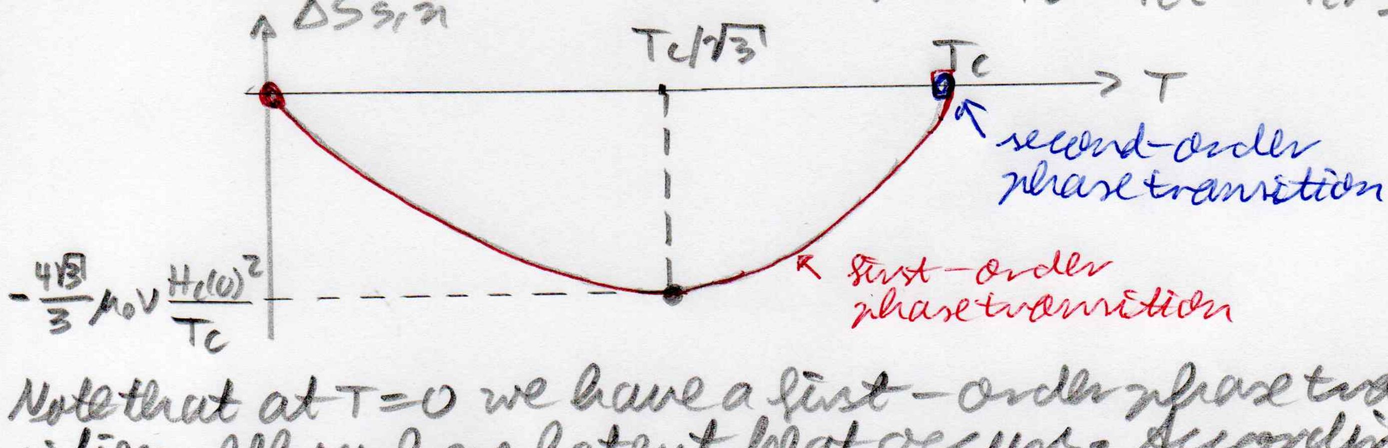
$$G_s(T,0)-G_n(T,0) = -\frac{\mu_0}{2}V H_c(0)^2\left[1-\left(\frac{T}{T_c}\right)^2\right]^2 \qquad (3.42)$$



The superconducting state has for $0 \le T \le T_c$ a lower free enthalpy than the normal conducting state.

3.7.2 Entropy:

For the difference of the entropies we obtain from (3.27) and (3.41): $S_s(T,0)-S_n(T,0) = -2\,\mu_0 V \frac{H_c(0)^2}{T_c}\frac{T}{T_c}\left[1-\left(\frac{T}{T_c}\right)^2\right]$ (3.43)

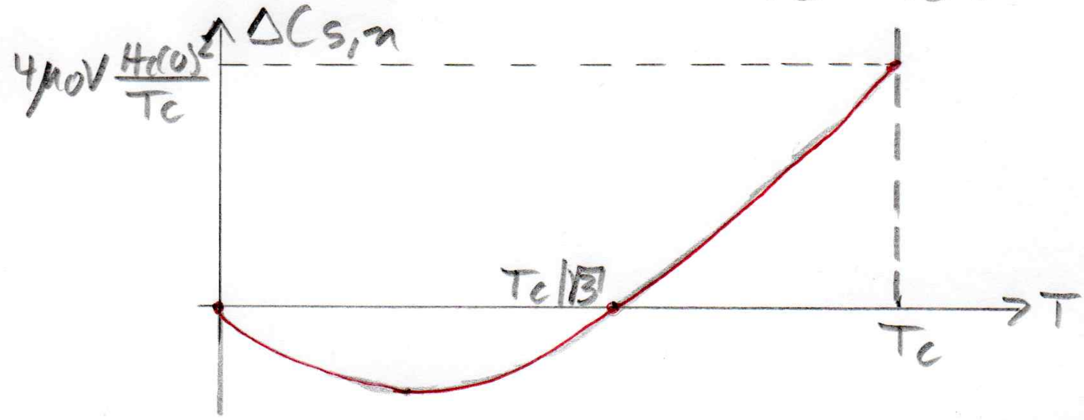


Note that at $T=0$ we have a first-order phase transition, although no latent heat occurs. According to the Ehrenfest classification just one first derivative of the thermodynamic potential must have a jump. And this jump occurs even at $T=0$, namely the magnetization jumps from $M_n=0$ in the normal conducting phase to $M_S=-H$ in the superconducting phase.

3.7.3 Heat Capacity:

The difference of the heat capacities is provided by the Rudgers formula (3.38) and (3.41):

$$C_S(T,0)-C_n(T,0)=2\mu_0 V\,\frac{H_c(0)^2}{T_c}\,\frac{T}{T_c}\left[3\left(\frac{T}{T_c}\right)^2-1\right] \quad (3.44)$$



Note that the negativity of the heat capacity difference (3.44) for $0<T<T_c/\sqrt{3}$ indicates that for low temperatures the superconducting heat capacity decreases faster than the normal conducting one. This is an indication of the presence of an energy gap in the superconductor.